

Spatial variation of wear and electrical properties across wrinkles in chemical vapour deposition graphene



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ABSTRACT

Chemical vapour deposition (CVD) is an effective and simple method for production of large area graphene needed for technological applications. However, CVD graphene contains a network of out of plane deformations - graphene wrinkles. Using atomic force microscopy (AFM) based methods, we find a significant change of graphene wear and electrical properties across the wrinkles. It is shown that graphene tearing by an AFM tip starts exactly from the wrinkles. Kelvin probe force microscopy shows that the surface potential of graphene is inhomogeneous, with domains within closed wrinkles having the surface potential different from the surrounding graphene. Conductive AFM shows that the electrical current drops exactly along wrinkles. Therefore, wrinkles decrease wear resistivity of graphene, they act as potential barriers for charge carriers leading to their localization, and lead to charge carrier scattering and increased contact resistance.

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1. Introduction

Potential technological applications of graphene are based on its excellent electrical, optical and mechanical properties. These applications include new platforms for flexible electronics, photonics, protective coatings, sensors, composite materials and biomedicine [1,2]. Graphene based technologies require large-area sheets, and they can not be based on the micrometre-size flakes obtained by the mechanical exfoliation. Chemical vapour deposition (CVD) is a simple and cost-effective method for the production of large-area graphene [3,4]. In this method, graphene is grown on metallic substrates, mostly on Cu foils [3] or thin nickel layers [4], and then transferred on a desired substrate [3–5].

However, in contrast to monocrystalline graphene samples obtained by the mechanical exfoliation, CVD graphene is a polycrystalline material. It consists of monocrystalline grains connected by grain boundaries [6–8]. Grain boundaries are a class of topological defects – they are one dimensional chains of aligned dislocations [8]. These defects inevitably influence graphene electrical and mechanical properties and degrade overall performance. Electrical resistivity is raised on grain boundaries [9–14], leading to

increased sheet resistivity of CVD graphene [15,16]. Scattering of graphene plasmons is enhanced on grain boundaries [17,18]. At the same time, fracture loads of CVD graphene are lower compared to monocrystalline graphene leading to decreased elasticity and strength [6,19–21].

Besides grain boundaries, CVD graphene contains a network of out-of-plane deformations - graphene wrinkles. The wrinkles appear either during the growth process or subsequent graphene transfer on a desired substrate [22,23]. Similar to grain boundaries, wrinkles have lower electrical conductance [24,25]. Generally, graphene corrugations lead to an inhomogeneous charge distribution [26–29]. Wrinkles in graphene lead to increased strain [30] and influence deformation of graphene sheets [31]. Wrinkles are chemically reactive so they are preferential nucleation centres for growth of organic molecules [32], they can serve for selective surface functionalization [33] or as nanosized gas inlets for reactions under graphene [34]. However, while the influence of grain boundaries on graphene electrical and mechanical properties is well investigated, so far the influence of graphene wrinkles is much less explored.

To tackle this problem, we investigate CVD graphene using atomic force microscopy (AFM). AFM based manipulation is used to study wear properties of graphene, whereas Kelvin probe force microscopy (KPFM) and conductive AFM (C-AFM) are used to study the surface potential distribution and the local conductivity in

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graphene, respectively. This paper discusses the influence of wrinkles on graphene properties. It is shown that graphene wrinkles decrease wear resistivity of graphene, since the graphene tearing by AFM tip starts exactly from the wrinkles. At the same time, electrical currents drop on wrinkles, while the surface potential is inhomogeneous, with localized charges within closed wrinkles.

2. Experimental

2.1. Sample preparation

Monolayer graphene films were synthesised in a cold walled CVD reactor using methane as the carbon source and copper foil (Alfa Aesar) as the metal catalyst. The thickness of the copper foil was 18 μm and they were annealed at 1000 $^{\circ}\text{C}$ using a hydrogen/argon atmosphere prior to the growth stage. The growth was carried out at 1000 $^{\circ}\text{C}$. Once the growth was complete the graphene was transferred onto the required substrates via a wet transfer process [3].

2.2. AFM measurements

All AFM measurements were done at ambient conditions using NTEGRA Prima system from NT-MDT. Imaging of CVD graphene was done in tapping mode using NSG01 probes from NT-MDT with typical tip curvature radius of 6 nm. Simultaneously with the topography imaging, the phase lag of AFM cantilevers was recorded.

AFM manipulation experiments [35] were done in order to study wear properties of graphene. Prior to the manipulation, AFM imaging was done in tapping mode. The manipulation was done in contact mode using DCP20 probes from NT-MDT. Hard and robust diamond coated probes DCP20 enabled both manipulation experiments and subsequent imaging. AFM manipulation was started by the scanning with the normal force around 0.5 μN . After every ≈ 20 scan lines, the normal force was increased by $\Delta F \approx 0.25 \mu\text{N}$. After the AFM manipulation experiments, the same area was imaged both in tapping mode and using C-AFM in order to characterize local changes in graphene morphology and electrical properties, respectively.

KPFM [36] was used in order to measure the contact potential difference (CPD) between an AFM probe and graphene [37]. Standard two-pass technique and nitrogen doped diamond coated probes DCP20 were used. In the first pass, a topography line was recorded in tapping mode. In the second pass, the probe was lifted by $h = 50 \text{ nm}$. AFM cantilever was electrically excited by the sum of a variable DC voltage and AC voltage with the frequency ω close to the cantilever resonance. CPD was then equal to the DC voltage which cancelled the cantilever oscillations at ω . Changes of CPD across graphene surface corresponded to changes of its electrical surface potential. Resolution for the surface potential measurements was 3 mV.

C-AFM was used to measure topography and local current simultaneously [38]. DC bias voltage was applied on graphene, while the scanning was done with nitrogen doped diamond coated probes DCP20. Local current–voltage (I – V) characteristics were measured in single point by recording currents through AFM probe during a ramping of the DC voltage in the range $\pm 2 \text{ V}$.

3. Results and discussion

3.1. Morphology

Three-dimensional topography of CVD graphene grown on Cu

foil is shown in Fig. 1 (a), whereas the corresponding phase image is given in Fig. 1(b). Graphene sheet is continuous and without cracks, while it follows the topography of the underlying Cu foil. It consists of rather flat Cu terraces (denoted with T in Fig. 1(a) and (b)) and Cu stairs (denoted with S in Fig. 1(a) and (b)). In the phase image, the stairs are clearly visible as bundles of curved and parallel lines. Here the huge phase contrast arises due to step heights in the topography of Cu foil.

Zoomed area with Cu stairs is shown in Fig. 2(a) (three-dimensional image) and 2(b) (two-dimensional image). Autocorrelation function of the two-dimensional topographic image is shown in Fig. 2(c), while the corresponding cross section is given in Fig. 2(d). Period of Cu stairs determined from the autocorrelation function is 424 nm. Similar values were obtained from other areas with Cu stairs. Both Fig. 2(a) and (b) show grain structure of Cu foil. The grain size is around 100–200 nm.

Topography and the corresponding phase image of the CVD graphene transferred on Si/SiO₂ substrate are shown in Fig. 3(a) and (b), respectively. Wrinkles are visible as bright lines in both topographic and phase images. Several largest wrinkles are denoted with arrows. Their directions are not related to each other. Wrinkles formed during the growth process originate from different thermal coefficients of Cu and graphene leading to larger shrinking of Cu foil during the postgrowth cooling [22]. On the other hand, wrinkles formed during the transfer process originate from substrate corrugations or residues from chemicals used in the transfer process [23]. Distribution of the wrinkles width and height is shown in Fig. 3(c). Narrow wrinkles are higher, and vice versa. Most of the wrinkles are 50–100 nm wide and 0.5–4 nm high.

Additional graphene corrugations are ripples distributed along arrays of curved lines. One such array is denoted with the wavy dashed line in Fig. 3(a) and (b). Similar quasi-periodic ripples in graphene have been already observed [39–42]. Zoomed graphene area is shown in Fig. 3(d). Arrows around the image show directions of the ripples. Distance between these lines is around 400–500 nm which corresponds quite well to the period of Cu stairs. Observed ripples should then correspond to the edges of Cu stairs.

In addition to wrinkles and ripples, whole CVD graphene sheet is slightly corrugated since it follows shape of Cu grains during the growth process, but it is not flat when transferred on Si/SiO₂ substrate. The average surface roughness of graphene is around 0.4 nm. It was determined from ten 500 $\times$ 500 nm² areas free from graphene wrinkles.

The island denoted with FLG in both topographic (Fig. 3(a)) and phase image (Fig. 3(b)) corresponds to few layer graphene (FLG) [3]. Its height is around 1 nm above single layer graphene sheet, so it

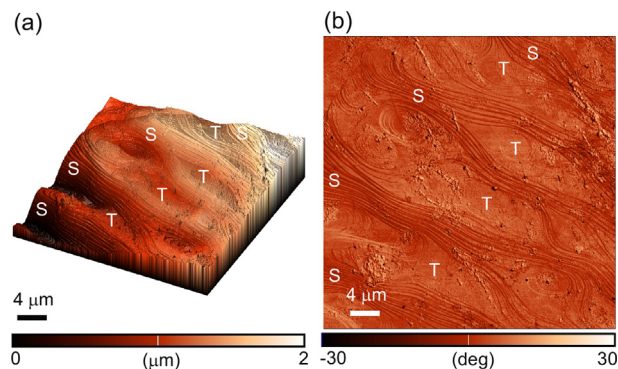


Fig. 1. CVD graphene grown on Cu foil: (a) topography and (b) phase image. T stands for Cu terraces, S stands for Cu stairs. (A colour version of this figure can be viewed online.)

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